

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
27 December 2001 (27.12.2001)

PCT

(10) International Publication Number  
**WO 01/98225 A1**

(51) International Patent Classification<sup>7</sup>: C03C 27/06

(21) International Application Number: PCT/US01/41042

(22) International Filing Date: 20 June 2001 (20.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/597,157 20 June 2000 (20.06.2000) US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:  
US 09/597,157 (CIP)  
Filed on 20 June 2000 (20.06.2000)

(71) Applicant (for all designated States except US): SCHOTT GLASS TECHNOLOGIES, INC. [US/US]; 400 York Avenue, Duryea, PA 18642 (US).

(72) Inventors; and

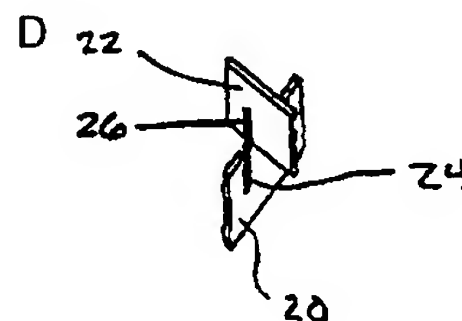
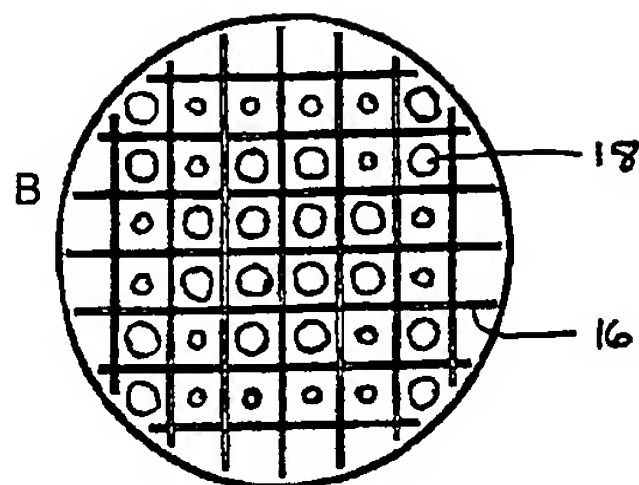
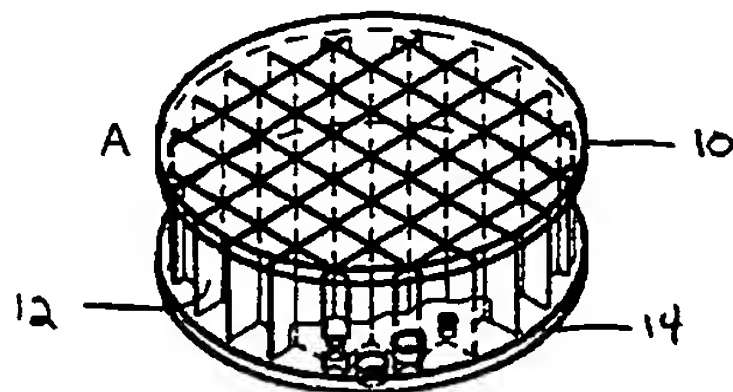
(75) Inventors/Applicants (for US only): CONZONE, Samuel, David [US/US]; 506 Glenburn Road, Clarks Green, PA 18411 (US). MARKER, Alexander, J., III [US/US]; Box 7176 RR7, Springbrook Township, PA 18444 (US).

(74) Agents: ZELANO, Anthony, J. et al.; Millen, White, Zelano & Branigan, P.C., Suite 1400, Arlington Courthouse Plaza 1, 2200 Clarendon Boulevard, Arlington, VA 22201 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,

[Continued on next page]

(54) Title: GLASS CERAMIC COMPOSITES



(57) Abstract: A method for joining glass ceramic surfaces to each other and/or other types of surfaces using a silicate liquid is disclosed. The products are suitable for use as, e.g. mirror blanks or microlithography stages, at low temperatures. Component pieces are polished then joined at low temperature using a silicate-containing joining liquid. Assembly is then performed in such a way that the joining liquid forms an interface between each component. After a period of low or slightly elevated temperature curing, rigid joints are formed throughout and the composite is dimensionally, vibrationally, and temperature stable and can withstand tensile stresses > 4000 psi. The room-temperature cured composite can be heat treated using a slow, systematic temperature increase to dehydrate the joints. A sealing coating may optionally be provided to prevent excess dried joining liquid from flaking off the formed joint.

WO 01/98225 A1



GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## Glass Ceramic Composites

### Background

#### 5 I. Field of the Invention

The invention relates to the field of glass ceramic composite structures and methods for forming composite glass ceramic structures using a low temperature joining process.

#### II. Description of the Prior Art

10 Glass ceramics, which generally consist of an inorganic, non-porous material having a crystalline phase and a glassy phase, are known for specialized applications. Such glass ceramics are manufactured by selecting suitable raw materials, melting, refining, homogenizing, and then hot forming the material into a glassy blank. After the glassy blank is cooled and annealed, a temperature  
15 treatment follows whereby the glassy blank is transformed into a glass ceramic by controlled volume crystallization (ceramization). Ceramization is a two-step process; nuclei are formed within the glass at one temperature, and then grown at a higher temperature. The dual structure of the glass ceramic material can impart very special properties, including a very low coefficient of thermal  
20 expansion (CTE).

One preferred material, Zerodur® (available from Schott Glass Technologies, Duryea, Pennsylvania) contains about 65-80 weight percent crystalline phase with a high quartz structure, which imparts a negative linear

thermal expansion. The remaining glassy phase (which surrounds the crystals) has a positive thermal expansion. The resulting behavior from the negative-CTE crystalline phase and the positive-CTE glassy phase is a material with an extremely low CTE.

5       Glass ceramics are useful in a wide variety of applications, such as mirror substrates for astronomical telescopes; mirror substrates for X-ray telescopes in satellites, optical elements for comet probes, weather satellites, and microlithography; frames and mirrors for ring-laser gyroscopes; distance gauges in laser resonators; measurement rods as standards for precision measurement  
10    technology, and other uses where very low CTE is important.

Large segments of monolithic glass ceramic are often used for many of the applications listed above. However, these large segments of monolithic glass ceramic are often very massive. For instance, larger astronomical telescopes can contain mirrors that exceed 3.6 meters, and the appropriate glass ceramic for use  
15    in such telescopes can exceed several tons. Thus, there is a need to develop light-weighted glass ceramic materials to overcome the problems associated with the massive nature of large monolithic segments of glass ceramic.

Various joining methods for optical materials are known; e.g. heat fusion, or frit bonding, however, none provides a low-temperature solution such as is  
20    provided for in the present invention.

The known prior art for fabricating light-weighted blanks (i.e. heat fusion, frit bonding) suffers from several drawbacks. For example, pressure and

temperature are typically required to form strong joints at high temperature. Developing loading/unloading fixtures for operation at  $T > 600^{\circ}\text{C}$  is complex and expensive. Further, heat fusion and frit bonding processes are conducted at temperatures near or above the glass transition temperature ( $T_g$ ) of the starting material (i.e., glassy Zerodur®, or ULE). The viscosity of glass is sufficiently low at these temperatures, such that limited flow (deformation) can occur. This deformation can cause gross dimensional changes, which can yield a defective mirror blank.

Additionally, large, high temperature furnaces (up to 2.0 m in diameter) with stringent thermal tolerances are required for heat fusion and frit bonding. Such furnaces must be custom-made and are often very expensive. Furthermore, glassy Zerodur® shrinks by approximately 3% during ceramization. This shrinkage can cause joint stresses that result in deformation and/or catastrophic failure of the mirror blank during joining.

Yet another difficulty encountered in the prior art is that light-weighted mirror blanks can fail during high temperature joining when thermally induced stresses form at the joint interfaces (especially during cooling to room temperature). Such joint failure results in a 100% loss after a tremendous amount of value has been added to the mirror blank (i.e., machining, polishing, water-jet cutting, assembly, high temperature fixturing, etc.).

A solution to this problem is needed, to allow for the low-temperature joining of fabricated mirror blanks in a step-wise manner.

### Brief Description of the Drawings

Figure 1A is a perspective view of a preferred embodiment of a lightweight mirror blank according to the present invention.

Figure 1B is a top plan view of a preferred embodiment of a lightweight  
5 mirror blank according to the present invention.

Figure 1C is a side view of a preferred embodiment of a lightweight mirror blank according to the present invention.

Figure 1D is a perspective view of a support element of a preferred embodiment of a lightweight mirror blank according to the present invention.

10 Figure 2 is a diagrammatic representation of the molecular structure of a surface of a glass ceramic material suitable for joining according to the present invention.

Figure 3 is a diagrammatic representation of the molecular structure of a joined glass ceramic material according to the present invention.

15 Figure 4 is a graphical representation of the average flexural strength of monolithic Zerodur® compared to various joined Zerodur® components.

Figure 5 is a graphical representation of the average CTE of joined Zerodur® rods.

Figure 6 is a diagrammatic representation of the vapor pressure build up  
20 between bulk Zerodur® blocks.

Figure 7 is a perspective view of a joined flexural sample.

Figure 8 is a perspective view of a joined CTE rod.

Summary of Invention

The present invention relates to a low-temperature process for the fabrication of lightweight composite glass ceramic structures, comprised, e.g., of a plurality (e.g., two or more) of glass ceramic components, said glass ceramic components each being polished sufficiently to form at least one joining surface on each component, providing a silicate-containing joining liquid to at least one of the joining surfaces, bringing the joining surfaces of the plurality of glass components together to form a joint, and allowing the joint to cure for a period of time at ambient temperature, whereby a cured joint is formed between said plurality of glass components. It also relates to a glass ceramic composite, comprising a plurality of glass ceramic components, said components being rigidly connected by a silicate-containing layer formed by curing a silicate-containing liquid between the glass ceramic components. The composites are preferably dehydrated by a carefully controlled dehydration process.

For example, a low-temperature process for the fabrication of lightweight composite glass ceramic structures, comprises:

providing a plurality of glass ceramic components, said glass ceramic components each being polished to form at least one joining surface on each component,

providing a silicate-containing joining liquid to at least one of the joining surfaces,

bringing the joining surfaces of the plurality of glass components together to form a joint,

allowing the joint to cure for a period of time of at least 20 hours at a temperature of at least 20 degrees C, whereby a cured joint is formed between  
5 said plurality of glass components, and

dehydrating the cured joint gradually by raising the temperature slowly and maintaining an elevated temperature below the glass transition temperature of the glass ceramic for at least 20 hours.

This invention also relates to:

10 A glass ceramic composite, comprising:

a plurality of glass ceramic components, said components being rigidly connected by a silicate-containing layer formed by curing a silicate-containing liquid between the glass ceramic components at a temperature of at least 20 degrees C for at least 20 hours;

15 A mirror blank suitable for use in space or flight applications comprising a plurality of glass ceramic components joined by a silicate-containing liquid and cured at a temperature of at least 20 degrees C;

A composite glass ceramic structure suitable for use as a microlithography stage comprising a plurality of glass ceramic components joined by a silicate-  
20 containing liquid and cured at a temperature of at least 20 degrees C;

A method of joining lightweight composite glass ceramic surfaces comprising applying to at least one of said surfaces a silicate-containing solution



and curing for an extended period at a slightly elevated temperature above room temperature; and

A light weight glass-ceramic mirror blank, comprising:

a face plate which is circular in shape,

5 a back plate which corresponds in shape and size to the face plate,

a plurality of support elements located between said face and back plates,

said plurality of supporting elements forming a latticework

said latticework and face plate and back plate defining a plurality of cells,

said cells each being provided with a ventilation aperture or being open to

10 the environment,

said face plate, plurality of supporting elements, and back plate being joined by a silicate-containing liquid in a plurality of joining steps to form a plurality of joints, and at each step, the joint cured at a temperature of at least 20 degrees C for a period of at least 20 hours.

15 A light-weighted mirror blank according to the present invention can be comprised of thin (preferably <5cm) face and back-plates that are fused, joined or bonded to a light-weighted core. Figures 1A, 1B, 1C, and 1D illustrate some of the separate components that may comprise a light-weighted Zerodur® mirror blank. While much of the description herein is in terms of the preferred  
20 Zerodur® material and mirror blanks, any glass ceramic material in general for any application is included in the invention.

With reference to Figure 1A, the face 10 and back plates 14 may be flat or curved sheets of Zerodur® that are polished on both sides. The light-weighted core may be a polished honeycomb-shaped component, which may be prepared by water-jet cutting segments from a solid slab of Zerodur®. It may also  
5 comprise supporting elements 12 arranged to support and space the face and back plates.

After assembly and fusion, a light-weighted mirror blank often has an overall mass/volume ratio that can be 30% of that for a standard (solid) Zerodur® blank, or even as low as 5 or 10% or even lower.

10 Figure 1B is a top view illustrating a preferred arrangement including the supporting elements 16 and ventilation holes 18.

Figure 1D illustrates a preferred way of joining two supporting elements 20, 22 using corresponding slots 24, 26. Optionally, the slots may be prepared with polished mating surfaces and joined according to the present invention.

15 Applicants have developed a novel method for fabricating composites, especially light-weighted glass ceramic mirror blanks and microlithography stages, at low temperatures. By low temperatures, as used herein, is meant temperatures generally under the glass transition temperature of the glass ceramic. Temperatures under 500°C may be suitable for practice of the  
20 invention, more preferably below 140°C, even more preferably below 130°C, most preferably, the temperature is  $\leq 120^\circ\text{C}$ . The light-weighted glass ceramic mirror blanks are intended for applications where dimensional stability,

adequate strength and low mass/volume are critical. Such applications include, but are not limited to, optical systems intended for space flight and airborne based applications such as satellites, navigation systems, and remote sensing, land-based systems, and precision structures such as microlithography stages.

5       The light-weighted structures according to the present invention should be rigid when compared to a monolithic piece of glass ceramic that the structures are replacing. By "rigid" is meant having essentially the same vibrational characteristics as the monolithic piece, being vibrationally, thermally, and otherwise dimensionally stable so as to have essentially indistinguishable opto-  
10       mechanical and thermo-optical characteristics from those of the monolithic piece of glass ceramic.

In a preferred embodiment, a low temperature joining technique is provided which allows light-weighted mirror blanks to be fabricated in a step-wise manner.

15       In a preferred embodiment, a polished face-plate, back-plate and light-weighted core are first prepared from the commercially available glass ceramic known as Zerodur®.

The polished components are cleaned in various aqueous and non-aqueous solutions before being dried and placed in a clean room environment.

20       A small volume of an aqueous based, silica-containing, joining liquid is applied to the polished joining surfaces of each component. Assembly is then performed in such a way that the joining liquid forms an interface between each

component (i.e., between the faceplate and the light-weighted core). After a period of room temperature curing, rigid joints are formed throughout the light-weighted mirror blank, which can withstand tensile stresses >4000 psi. Furthermore, the dimensional stability of the joined mirror blank is similar to  
5 that of pure, monolithic Zerodur® (i.e., the coefficient of thermal expansion of the blank is < 75 ppb/K, is unaffected by the joining, and is the same as the monolithic glass ceramic that is being replaced). Such room-temperature-cured mirror blanks are then preferably heated to temperatures ranging from 60 to 120°C to promote joint dehydration and accelerate the curing process.

10 In a particularly preferred embodiment, the joints are subjected to an extended duration of slight temperature increase to dehydrate the joints. The removal of water from the joints over an extended period of time dramatically increases the strength, reliability, and rigidity of the structures according to the present invention over the strength, reliability, and rigidity of joints that are  
15 quickly dehydrated (e.g. by microwave). Preferable temperatures for the extended duration dehydration include from 20-50 degrees C for at least 20 hours, more preferably from 30-40 degrees C for at least 20 hours up to three weeks.

Several advantages arise out of the novel low-temperature joining process.  
20 First, a light-weighted mirror may now be constructed piece by piece, thus eliminating some of the risk associated with the high temperature processes. During high temperature processing the entire mirror blank could deform

during heating or fracture during cooling, with no indication until furnace unloading. Second, a drying furnace capable of temperatures up to  $\approx 120^{\circ}\text{C}$  may be required for low-temperature joining. Such low temperature drying furnaces are commercially available and much less expensive than high temperature  
5 furnaces. Third, no material deformation occurs, since low temperature joining is conducted at temperatures well below the  $T_g$ , where glass ceramics are elastic solids. Fourth, fully ceramized glass ceramics are utilized for low temperature joining. This eliminates the problems associated with the shrinkage that occurs when the glass is converted to a glass ceramic during heat fusion. Fifth, pressure  
10 is not typically required for low temperature joining. Thus, no complicated loading/unloading fixtures are necessary.

These and other advantages will become apparent to one of skill in the art having regard for this disclosure.

A lightweight mirror blank represents a substantial investment of time  
15 and materials, which makes the mirror blank very expensive. If a defect arises or a catastrophic failure occurs within the unit during high temperature bonding (e.g. heat fusion or frit bonding), the entire value-added process is a loss and the process must start anew. The applicants have developed a novel process which provides for the component by component assembly of large, light-weighted  
20 structures, and may be accomplished at low temperatures (i.e. well below the  $T_g$  of typical alkali-alumino silicate glasses,  $< 500^{\circ}\text{C}$ ).

Glass ceramics that are joined according to the instant invention are first prepared by selecting the monolithic pieces to be fabricated into a finished composite structure. Various elements, e.g. mirror components, face plates, back plates, and structural connections are fabricated and sized to yield a composite,  
5 light-weighted structure which has a low thermal expansion.

A light-weighted mirror blank, for example, as used herein, is a physical structure onto which a reflective coating may be applied to form a functional mirror. Mirrors are typically used during flight or space applications where remote sensing is being conducted. Satellites which image portions of the earth's  
10 surface, or other space-based observation platforms use such mirrors. A high level of stability, structural and thermal, is required to obtain an acceptable image. Space-based applications may be exposed to extremes in temperature, which require an extraordinarily reliable and sound structure.

Glass ceramics are suitable materials for such applications, since they  
15 exhibit excellent stability during temperature fluctuations. One such glass ceramic is Zerodur®, which is an example of an especially preferred mirror blank material because it has excellent dimensional stability, owing to a CTE of less than 75 ppb/K from 0 - 50 °C. Other glass ceramics, based on SiO<sub>2</sub> - containing glasses, including Nexcera, a glass ceramic made by Nippon Steel,  
20 Tokyo, Japan, VO<sub>2</sub> or V<sub>2</sub>O, a lithium alumino silicate glass ceramic produced in VR China Xinhua Factory, Shanghai, China, Clearceram, Astro-Sitall and Sitall,

which are lithium alumino silicate glass ceramics produced by Lytkarino, Moscow, Russia are suitable for the practice of this invention.

Normally, monolithic (i.e. solid) mirrors are utilized to fabricate precision optics due to their ease of manufacture, dimensional stability, and excellent mechanical strength. A monolithic mirror blank is fabricated from a single piece, having no joints, and such mirror blanks are usually massive structures. For example, a standard, cylindrical Zerodur® mirror blank with a diameter of 1.5 m and a thickness of 0.25 m will have a mass of greater than 1,100 kilograms (i.e. greater than 2,400 pounds). Lifting and/or automating such a massive weight often prevents the use of glass ceramic mirror blanks in flight or space-based applications.

The present invention enables a series of components to be assembled, and can overcome the drawbacks associated with the large mass of monolithic mirror blanks. Lightweight mirror blanks, which preferably consist of thin (preferably less than 5 cm) face and back plates, that are attached to a light-weighted core, as shown in Figure 1. These three components, i.e. face plate, back plate, and light-weighted core, are joined according to the present invention to form a stable, rigid, light-weighted mirror blank at low temperature.

With reference to Figure 1, a novel light-weighted mirror blank according to the present invention is seen. The outer surfaces of the mirror blank may be flat, curved, concave, convex, or any geometrically desired shape. The face and

back plate are preferably between 0.5 cm and 5 cm in thickness, most preferably about 1-3 cm thick.

Beneath the face plate (from the perspective of figure 1) is a lattice of supporting elements 12 forming a light weighted core. Each of these elements is also preferably a glass-ceramic to yield a uniform coefficient of thermal expansion for the unit. The supporting elements are illustrated as aligned in a crosshatched manner, but any suitable arrangement, which provides dimensional stability, is acceptable. The supporting elements are preferably designed for sufficient stability without excessive weight. The elements may have voids drilled within (e.g. by water cutting or mechanical drilling) to further reduce the mass of material. Other shapes and styles of supporting elements may be designed by one of skill in the art having regard for this disclosure.

In an alternative embodiment, the light-weight core is formed from monolithic Zerodur® by water-jet cutting, ultrasonic drilling, laser cutting, diamond saw drilling, etc.

When such a light weight mirror blank is finished, the overall mass may be reduced by as much as 70% or more when compared to a monolithic structure, yet retaining sufficient CTE and strength characteristics to be perfectly suitable for airborne or space borne applications where high tolerances are expected.

Appropriate components (including a face plate, back plate, and light weighted core) should be selected to obtain the maximum benefits of the instant



invention. For example, a plurality of components to be fabricated into a larger structure would be selected as follows.

A plurality of components of glass ceramic with nearly identical CTE's are selected. By way of example, three slabs of Zerodur™ with nearly identical CTE  
5 (i.e., each within  $\pm 25$  ppb/K) will be fabricated. In this example, a 30 cm mirror blank is to be fabricated.

Two slabs will have nominal dimensions of 30 cm in diameter and 3 cm thick. These two slabs will form the face and back-plates of a light-weighted mirror blank according to the instant invention. The third slab will have a  
10 diameter and thickness of approximately, 30 cm and 4 cm, respectively. This third slab will be used to fabricate the light-weighted core.

The two slabs intended for the face and back-plates are cut and/or ground to an appropriate thickness, and then polished. The surfaces intended for joining are prepared with a surface figure of  $1/3 \lambda$  ( $\approx 200$  nm peak to valley). Although  
15 the face and back-plates may be flat, other geometric shapes are possible (i.e., they may be concave, convex, or of other suitable shape).

A plurality of holes are drilled through the back-plate to reduce the overall weight of the mirror blank, and to provide an opening for each cell within the light-weighted core.

20 The slab intended for the light-weighted core is cut and ground to an appropriate thickness and then polished. Both surfaces of the core have a surface figure of  $1/3 \lambda$  ( $\approx 200$  nm peak to valley). Again, the core may be flat or of other

geometric shape (i.e., either side could be concave, convex, or other suitable shape as appropriate to provide surfaces that will "mate" with the face and back plates during assembly).

The core is then weight-reduced by removing excess material without  
5 compromising the structural integrity of the core. For example, it may be converted into a honeycomb-like shape by water-jet cutting, or any other method in the cutting art that can be used to transform a solid piece of glass into a honeycomb-like structure (i.e., laser cutting, ultrasonic drilling, drilling and cutting with conventional equipment, etc.). The machined core will be referred  
10 to as the light-weighted core hereafter. If necessary, the surfaces of the light-weighted core are re-finished to remove any surface damage that results from the weight reducing step.

After the component pieces are selected and prepared, the next step of the instant novel process preferably includes cleaning. Each component (face-plate,  
15 back-plate, light-weighted core) is, if necessary, cleaned simultaneously or independently, using the following procedure:

First, the components will be immersed in a cleaning solution comprised of 10 vol% Micro Solution and 90 vol% deionized H<sub>2</sub>O for approximately 30 minutes. This solution is preferably agitated by stirring, rocking, vibration or  
20 forced circulation. The cleaning solution is then removed and the component immersed in deionized H<sub>2</sub>O for approximately 5 minutes.

The component is then removed from the  $\text{H}_2\text{O}$  and immersed in a  $\text{KOH}_{(\text{aq})}$  solution (0.01 to 9.0 M) for approximately 5 minutes. Subsequently, the components are removed from the  $\text{KOH}_{(\text{aq})}$  solution and immersed in deionized  $\text{H}_2\text{O}$  for approximately 5 minutes.

5        Finally, each component is rinsed with high purity (low residue) ethanol, then rinsed with high purity (low residue) methanol, and transported into a clean room environment. After transporting the components into the clean room, deionized  $\text{N}_2$  gas will preferably be used to remove any residual methanol from the joining surfaces. Optionally, a  $\text{CO}_2$  sno-gun is used to remove any dust  
10    or particulate debris from the joining surfaces.

At this point, all joining surfaces are chemically clean and free from particulate debris. The clean, dry components are then stored, such that their joining surfaces are not in contact with any source of particulate or chemical contamination.

15        Once the component pieces are polished and cleaned to the requisite degree, the surfaces to be joined should be free of debris and contain a large concentration of silanol ( $\text{Si-OH}$ ) groups, as may be seen in figure 2.

An exemplary silicate "joining liquid" with the general oxide composition shown in Table I is prepared and is used for low temperature joining according  
20    to the present invention. The joining liquid typically contains silanol ( $\text{Si}(\text{OH})_4$   $_{(\text{aq})}$ ), alkali ( $\text{Na}^+_{(\text{aq})}$ ) and other aqueous species (i.e.,  $\text{H}_2\text{O}_{(\text{aq})}$ ,  $\text{H}_3\text{O}^+_{(\text{aq})}$ ,  $\text{OH}^-_{(\text{aq})}$ ). Although not wishing to be bound by the theory of joint formation, the notations

under "comments" give a theoretical explanation for the functionality of species in the joining liquid.

Table I: Compositional Space for the Joining Liquid

Oxide Component	Wt%	Comments
H <sub>2</sub> O	50-99.9	H <sub>2</sub> O is the solvent, and H <sub>2</sub> O molecules may contribute to joint strength by forming hydrogen bonds across the joint interface
SiO <sub>2</sub>	0.01-40	The SiO <sub>2</sub> component of the liquid is primarily responsible for joint rigidity (i.e., -Si-O-Si cross links)
Al <sub>2</sub> O <sub>3</sub>	0-10	Al <sub>2</sub> O <sub>3</sub> could be added to the liquid to increase the chemical durability of the resulting joint, and to make the interfacial region more chemically similar to Zerodur™ (a lithium alumino-silicate glass ceramic)
Li <sub>2</sub> O	0-20	Li <sup>+</sup> ions could contribute to joint strength by forming Li <sup>+</sup> /NBO (non-bridging oxygen, SiO <sup>-</sup> ) bonds.
Na <sub>2</sub> O	0-20	Na <sup>+</sup> ions could contribute to joint strength by forming Na <sup>+</sup> /NBO bonds.
K <sub>2</sub> O	0-25	K <sup>+</sup> ions could contribute to joint strength by forming K <sup>+</sup> /NBO bonds.
MgO	0-10	Mg <sup>2+</sup> ions could contribute to joint strength by forming Mg <sup>2+</sup> /NBO bonds.
CaO	0-10	Ca <sup>2+</sup> ions could contribute to joint strength by forming Ca <sup>2+</sup> /NBO bonds.
BaO	0-10	Ba <sup>2+</sup> ions could contribute to joint strength by forming Ba <sup>2+</sup> /NBO bonds.
SrO	0-10	Sr <sup>2+</sup> ions could contribute to joint strength by forming Sr <sup>2+</sup> /NBO bonds.

5 Other suitable joining liquids include lithium silicate liquid, potassium silicate liquid, magnesium silicate liquid, calcium silicate liquid, barium silicate liquid, strontium silicate liquid, mixed alkali silicate liquid, mixed alkali/alkaline earth silicate liquid, mixed alkaline earth silicate liquid, and silicate liquid, where "liquid" refers to an aqueous solution.

Joining is initiated by sandwiching the appropriate liquid between two clean surfaces, as shown in Figure 3. Only a small volume ( preferably  $\approx 0.5 \mu\text{l}/\text{cm}^2$ ) of the joining liquid is required to form a strong joint. Larger or smaller volumes may be used by one of skill in the art having regard for this disclosure.

5 It is preferred that at a minimum there be at least  $0.01 \mu\text{l}/\text{cm}^2$ .

In another embodiment of the present invention, ground or fritted glass-ceramic or glass, *e.g.*, Zerodur® or silica-containing glass or glass-ceramic, could be added to the joining liquid to form a stronger joint, fill in voids at the joint interface, and promote joint dehydration.

10 A joining liquid with the general composition shown in Table I is used to join the face and back plates to the light-weighted core. First, particulate debris is preferably removed from the joining liquid using filtration and/or centrifugation. The two joints required to fabricate a light-weighted mirror blank (face-plate to light-weighted core, and back-plate to light-weighted core)  
15 could be fabricated simultaneously, but preferably they are fabricated separately.

Joining liquid is applied to one or both surfaces intended for joining (*i.e.*, to the back of the faceplate and the mating side of the light-weighted core) by any of a number of coating techniques. For example, spin coating may be used, where an excess of joining liquid is to be applied to the surface, and then the  
20 majority removed by high-RPM spinning.

Another application technique is dip coating, where the surface is dipped into a vat of joining liquid of appropriate viscosity and then removed at an

appropriate speed to ensure that an adequate volume (at least 0.01  $\mu\text{l}/\text{cm}^2$ ) of joining liquid remained.

Another suitable method is pipetting or auto-dispensing drops of joining liquid at various points on the joining surface. Upon joining, these drops would  
5 spread and provide an adequate volume of joining liquid. Yet another method contemplated by the instant invention includes joining the components while submerged in a vat of joining liquid, i.e. assembling the mirror blank while submerged. Another method includes bringing the two components into contact and allowing the joining liquid to be introduced from the side and be  
10 drawn between the two surfaces to be joined by capillary action. Capillary forces will "pull" the liquid into the interfacial region and a joint will be formed.

One skilled in the art having regard for this disclosure may envision the use of any automated technique commonly used to dispense liquid in, e.g., the adhesives industry. In a preferred embodiment, reproducible volumes of joining  
15 liquid are applied to the joining surfaces.

In an especially preferred embodiment, premature curing (hardening) of the liquid prior to joining is avoided by performing the joining in a humid environment. The silicate liquid quickly dries under a dry atmosphere (<30% relative humidity) to form a residue, which results in an imperfect joint.

20 For example, when making a joint at a low relative humidity <30% RH, the following problems can occur:

- 1) Premature drying of the joining liquid resulting in a thick joint interface >>1 micron.
- 2) Premature drying of the joining liquid resulting in joint turbidity.
- 3) Premature drying around the edges of a drop of joining liquid that is  
5 applied to the joining surface resulting in a ring-shaped defect at the joint interface.
- 4) Debonding after curing at room temperature.
- 5) Debonding after heat treatment at temperatures ranging from 30°C to 600°C.
- 10 6) Premature drying of the joining liquid resulting in the inability to align the pieces once in contact.
- 7) Near impossibility of evenly coating a complicated light weighted structure prior to joining without encountering problems mentioned above.

The problem is intensified as the volume of joining liquid is reduced (for  
15 instance from 0.5 $\mu$ L/cm<sup>2</sup> to 0.05 $\mu$ l/cm<sup>2</sup>).

In order to minimize these problems and to achieve defect reduced, strong joints, bonding should be conducted in a controlled humidity environment ranging from about 30% R.H. to about 100% R.H., preferably from about 60% R.H. to about 100% R.H., more preferably from about 75% R.H. to about 95%  
20 R.H. A particularly preferred condition is at about 80% relative humidity. A suitable time period range between solution application and bonding contact of the surface, *i.e.*, bonding, is from immediately after application to about 10

minutes after application, preferably from immediately after application to about 5 minutes after application, more preferably from immediately after application to about 1 minute after application. It is particularly preferred to contact the surfaces as soon as possible after solution application.

5           In a preferred embodiment, the faceplate is brought into contact with the light-weighted core using an alignment apparatus. The joining liquid forms an interface between the two clean, polished (*e.g.*, course or finely ground) surfaces. The joined component should be allowed to cure for at least 1 hour before attempting to fabricate the second joint.

10           After allowing at least 1 hour for the first joint (face plate to light-weighted core) to cure, joining liquid will then be applied to the back plate. The back plate is then brought into contact with opposite side of the light-weighted core using an alignment apparatus. The joining liquid then spreads and forms an interface between the two components. In an especially preferred embodiment,  
15   each hole in the back-plate is aligned with each cell (void) in the light-weighted core.

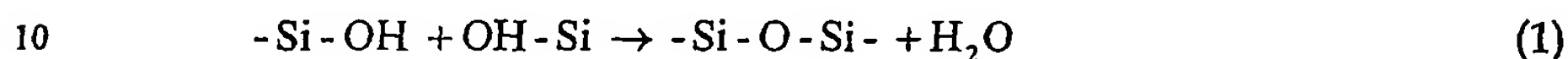
Aligning the holes in the back-plate with the cells in the light-weighted core ensures that no air is trapped within the light-weighted mirror. Trapped air can be problematic, especially when the mirror blank is used for an application  
20   where appreciable temperature fluctuation can occur. Temperature fluctuations would change the air pressure within an airtight compartment and could cause



local variations in the surface figure of the front faceplate. Such local variations in surface figure could compromise the performance of the mirror.

Although not wishing to be bound by the following theoretical explanation, it is believed that the following mechanism explains the development of such mechanically strong, low CTE joints by the low-temperature joining process.

Once the liquid is sandwiched between the two surfaces, condensation reactions (Equation (1)) begin as silanol groups combine to form -Si-O-Si- linkages, while releasing (condensing) H<sub>2</sub>O.



A rigid joint is formed when the -Si-O-Si- cross-linking spreads throughout the interfacial region and eventually binds the two joining surfaces together, as shown in figure 3. The resulting joint is composed of a hydrated, silicate solid. It is a sodium silicate solid if a sodium silicate liquid is used for the joining process.

It is believed that the Si-O-Si- linkages are primarily responsible for joint strength. While the H<sub>2</sub>O present in the interfacial region (i.e., that formed by condensation reactions and that originally present in the joining liquid) can evaporate from the joint interface, diffuse into the joining material, or form hydrogen bonds across the interface, it is believed that H<sub>2</sub>O can also contribute to the overall joint strength. Finally, the Na<sup>+</sup> ions are expected to form chemical bonds between non-bridging oxygen (NBO) atoms within the joint interface. The

result of -Si-O-Si- cross-linking, hydrogen bonding and Na<sup>+</sup>/NBO bonding is a rigid joint that typically has a strength  $\geq 4000$  psi.

The residual H<sub>2</sub>O that remains in the interfacial region after room temperature curing may contribute to the overall joint strength by providing  
5 hydrogen bonding. However, in an alternative embodiment of the present invention, the joint is dehydrated. If, for example, the end application for the joint requires stability at temperatures  $>100^{\circ}\text{C}$ , removal of H<sub>2</sub>O will reduce the risk of failure.

The fully joined, light-weighted mirror blank would be allowed to cure at  
10 room temperature for at least 1 day, and preferably for 7 days before a dehydration should be attempted.

Not all forms of dehydration will work in preparing joints according to the instant invention. For example, when Zerodur® - Zerodur® joints are prepared at room temperature and then subjected to microwave treatment,  
15 catastrophic failure generally occurs. Dehydration without catastrophic failure can best be achieved by using a slow, controlled heat-treatment schedule according to the present invention.

When small samples of glass-ceramic Zerodur® (30x20x10 mm, joining surface 10x10 mm) are fabricated according to the present invention, after 1-week  
20 room temperature cure, these joints are strong enough that they cannot be fractured by hand.

When excessive force is applied, the resulting fracture does not necessarily occur at the joint interface. When small Zerodur® - Zerodur® samples are fractured by impacting them on a hard surface, the fracture often results in pullout of material on either side of the joint interface. Zerodur® - Zerodur® joints formed at room temperature according to the instant invention show excellent strength characteristics as evident from the flexural strength testing results shown in Figure 4. A room temperature cured Zerodur® - Zerodur® joint has a flexural strength, which can exceed 9,000 psi.

The large flexural strengths (5,000 to 10,000 psi) achieved by joining and curing Zerodur® at room temperature are sufficient for space-based applications (where the allowable stress for Zerodur® is 750 psi). However, the strength and stability of such room-temperature-cured joints is deleteriously affected by temperature ramps ( $>10$  K/h).

Quickly heating room temperature cured Zerodur® - Zerodur® joints to temperatures  $>50^{\circ}\text{C}$  (i.e., by subjecting the joint to excessive microwave radiation) will often cause catastrophic failure. Although not wishing to be bound by this theory, it is believed that residual  $\text{H}_2\text{O}$  at the joint interface is likely responsible for the strength degradation and proneness for failure when Zerodur® - Zerodur® joints are quickly heated.

When a room temperature cured, Zerodur® - Zerodur® joint is heated at  $>10$  K/h to temperatures  $>50^{\circ}\text{C}$ , the vapor pressure of  $\text{H}_2\text{O}$  within the hydrated joint interface is increased. This increase in vapor pressure cannot necessarily be

accommodated by H<sub>2</sub>O diffusion into the bulk Zerodur®. As noted previously, Zerodur® is a glass ceramic, which contains ~70 wt% of ~50 nm lithium aluminosilicate crystals in a matrix of silica-rich glass.

Most diffusion models for glass-ceramics assume that the crystalline phase  
5 is impermeable to diffusing species, such as OH<sup>-</sup>, H<sub>3</sub>O<sup>+</sup> or H<sub>2</sub>O. Thus, the crystalline nature of Zerodur® likely blocks H<sub>2</sub>O diffusion into the bulk, and it is believed that the only way for H<sub>2</sub>O to escape the hydrated joint interface is by surface diffusion to the edge of the sample, see Figure 6. Once the H<sub>2</sub>O reaches the edge of the joint, it can easily be removed by evaporation.

10 When a Zerodur® - Zerodur® joint is rapidly heated, and the vapor pressure within the joint interface is not offset by H<sub>2</sub>O surface diffusion, interfacial damage or joint failure can occur. Interfacial damage is generally apparent in the form of small (1mm) bubbles that form at the joint interface. Such damage usually occurs when a room-temperature-cured, Zerodur® -  
15 Zerodur® joint is heated at ≥5 K/h in a furnace or oven. Sufficiently rapid heating (i.e., subjecting a room temperature cured Zerodur® - Zerodur® joint to microwave radiation, in a commercial microwave oven) often causes catastrophic failure, as the joint simply "pops" apart.

A novel slow and systematic heat-treating technique has been developed  
20 to dehydrate room-temperature-cured glass-ceramic and Zerodur® - Zerodur® joints. The heat-treatment schedule is shown in Table II. This heat-treatment schedule is suitable for joint dehydration where the mean free path for H<sub>2</sub>O

surface diffusion is preferably no greater than 12.5 mm. This exemplary treatment schedule is a preferred schedule; slower treatments are possible and may be preferable for different types of joints. Such treatment regimens may be easily developed by one skilled in the art having regard for this disclosure.

5

**Table II: Preferred Heat Treatment Schedule for Dehydrating 25x25 mm Joints**

Step	Ramp Rate (K/h)	Temperature (°C)	Hold (h)
1	0.001 - 2	40	10 - 40
2	0.001 - 3	50	15 - 60
3	0.001 - 3	60	20-80
4	0.001 - 3	70	20
5	0.001 - 3	80	20
6	0.001 - 3	90	20
7	0.001 - 3	100	20
8	0.001 - 3	120	20

The strength of heat-treated Zerodur® - Zerodur® and other glass-ceramic joints may be slightly less than those cured at room temperature (Figure 4), and this is likely due to the depletion of hydrogen bonding at the joint interface (as H<sub>2</sub>O is removed by evaporation). However, the strength and dimensional stability of such heat-treated joints are more than sufficient for use in light-weighted mirror blank applications and others requiring at least 750 psi strength. Figure 4 shows that the flexural strength of Zerodur® - Zerodur® joints is always at least five times greater than the allowable stress for Zerodur®, regardless of heat-treatment temperature from 60 to 120°C. Furthermore, the dimensional stability does not seem to be affected by heat-treatments up to

120°C, since the CTE of Zerodur® - Zerodur® joints were not statistically different from the average CTE of a monolithic Zerodur® slab (i.e.,  $-26 \pm 10$  pb/K) as shown in Figure 5.

Heat-treatment at temperatures above 120°C may further increase the strength of a Zerodur® - Zerodur® joint. The interfacial region that joins two Zerodur® sections together is essentially a sol-gel derived material (i.e., the sodium silicate liquid (sol) was transformed to a rigid interfacial region (gel) by curing). Sol gel materials derived from sodium silicate liquid can be heat-treated at temperatures exceeding 600°C, to increase the density and strength. However, the primary goal of a low-temperature joining process is to avoid as much excessive heat treatment as is possible.

In yet another preferred embodiment, such joined components may be overcoated with a polymeric coating to prevent the loss of dried joining liquid after the joint has been cured. In many applications, the avoidance of particulate debris, such as flaked off dust, is highly desirable and the addition of a polymeric or other sealant coating is preferred.

Although the foregoing discussion has been framed in terms of joining two or more glass ceramic structures, it is also possible to join a glass ceramic surface to other types of surfaces using the same procedures and considerations discussed above. Suitable other surfaces which can be joined to glass ceramic surfaces using the same silicate joining liquid and considerations include surfaces of a glass, metallic, metallic alloy, crystalline, polymeric, etc. nature.

Typically, a surface can be joined to a glass ceramic surface in accordance with this invention as long as it has surface reactive groups which react with components of the joining liquid to form bonds to both surfaces, *e.g.*, which permit the formation of Si-bonds with the silicon atoms in the joining liquid, *e.g.*,  
5 via -O-, -N-, -C-containing, -P- etc. bonds, *e.g.*, surface OH, NH<sub>2</sub>, PO<sub>4</sub>, etc. groups, or carbonaceous groups containing, *e.g.*, -O- or -P- atoms, etc. Suitable such surfaces include, for example,

- SiO<sub>2</sub> (glass, non crystalline)
- quartz
- 10 -Al<sub>2</sub>O<sub>3</sub> (aluminum oxide, crystalline)
- multi component silicate glass
- BK-7
- ULE, a titanium silicate glass produced by Corning, Inc, Corning New York
- antimony silicate glasses
- 15 -low expansion metallic alloys (*e.g.*, Invar) optionally coated with a thin layer of SiO<sub>2</sub>
- germanium glasses
- tellurium glasses
- borosilicate glasses

20

Thus, where a glass substrate is used, it is preferably a multi-component oxide glass, a non-oxide glass, or a mixed oxide glass. Preferred multi-component oxide glasses include silicate, borate, germanate, telluride, phosphate or aluminate glasses. Preferred non-oxide glasses are chalcogenide, fluoride, heavy  
25 metal fluoride (*e.g.*, ZBLAN®) or sulfide (*e.g.*, As<sub>2</sub> S<sub>3</sub>) glass. A preferred mixed oxide/fluoride glass is a fluorophosphate glass. Where a crystalline material is used it is preferably a single crystalline material, *e.g.*, a non-semiconducting material such as LiNbO<sub>3</sub>, a fluoride such as CaF<sub>2</sub> or LiF, a chloride such as NaCl

or AgCl, an iodide such as KI, a bromide such as AgBr, or an oxide such as Sapphire ( $Al_2O_3$ ). Alternatively, the single crystalline material may be a semiconducting material such as GaAs, InP, ZnS, ZnSe, ZnTe, Si or Ge.

For joints to surfaces other than glass ceramics, the rate of heat treatment  
5 discussed above can be modified according to the nature of the non-glass ceramic surface. For example, for glasses such as silica and other materials which have open networks through which water can escape from the joint interface or which are hygroscopic (*e.g.*, phosphate later glasses) rates higher than the approximate value of  $5^\circ K/hr$  mentioned above may be applicable, *e.g.*,  
10 6, 7, 8,  $10^\circ K/hr$  etc., depending on the substances involved. Routine experiments will readily determine suitable values.

Moreover, the nature of the non-glass-ceramic material will also straightforwardly affect the temperature of heating. When glasses are joined, the maximum temperature should not exceed the lowest glass transition  
15 temperature of the jointed materials. Analogously, the maximum temperature should not exceed any value which would adversely affect the properties of the joined materials. For example, when one material has a CTE lower than the others, routine care will be taken to ensure that temperatures are avoided which would cause one or more bonded surfaces to rupture or be stressed  
20 unacceptably.



Although the foregoing discusses primarily mirror surfaces, virtually any kind of device can benefit from this invention's surface joints, e.g., also etalons, vacuum chambers, low expansion structures in general, etc.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius; and, unless otherwise indicated, all parts and percentages are by weight.

The entire disclosures of all applications, patents and publications, cited above, and U.S. Serial No. 09/597,157 filed June 20, 2000, are hereby incorporated by reference.

15

## EXAMPLES

### Example 1

Zerodur® samples with approximate dimensions of 60x25x25 mm were used for all joining experiments. One of the 25x25 mm faces on each sample was polished, with a surface figure of at least  $1/3 \lambda$  (200 nm peak to valley, this surface will be referred to as the joining surface), while the other 25x25mm face was simply polished to a transparent finish.

The joining surfaces were cleaned using various solutions. First, the samples were ultrasonically cleaned in a 10:90 volumetric ratio of Micro Cleaning Solution and deionized H<sub>2</sub>O. The samples were then rinsed with deionized H<sub>2</sub>O before being ultrasonically cleaned with 3.0 M KOH<sub>(aq)</sub> solution. After cleaning  
5 with KOH<sub>(aq)</sub> solution, the samples were rinsed with deionized H<sub>2</sub>O, ethanol and methanol before being dried with deionized N<sub>2</sub> gas. Finally, a CO<sub>2</sub> sno-gun was used to remove particulate debris from the joining surfaces. The clean samples were placed within a clean, dust-free enclosure until joining was conducted.

The Zerodur® samples were joined using a low temperature joining process.  
10 When making a joint by the low temperature joining process, sodium silicate liquid is sandwiched between two clean, polished, joining surfaces. A mechanically strong joint is formed when the liquid cures and forms a rigid interface between the two joining surfaces.

A sodium silicate liquid containing ≈15 wt% SiO<sub>2</sub> and ≈6 wt% Na<sub>2</sub>O was used  
15 for all Zerodur® - Zerodur® joining experiments conducted for strength evaluation. The joining liquid was prepared by diluting commercially available sodium silicate liquid with deionized water. After dilution, the resulting liquid was filtered with a 0.2 μm filter, before centrifugation was used to separate and remove any remaining particulate debris. A 3 μl drop of the centrifuged sodium  
20 silicate joining liquid was applied to the joining surface of a Zerodur® sample using a pipette. A second joining surface was then brought down upon the 3 μl drop to spread and sandwich the joining liquid between the two Zerodur™

surfaces. All of the joining experiments were conducted in a clean, dust free enclosure.

The joint assembly (two 60x25x25 mm samples joined with the sodium silicate liquid) was allowed to cure for at least 7 days at room temperature (15 to 30°C).

5 Some joint assemblies were also heat-treated at temperatures ranging from 60 to 120°C. Flexural samples were machined from the room temperature cured and heat-treated joint assemblies, as shown in Figure 7.

Care was taken during machining to ensure that the samples were not subjected to elevated temperatures ( $> 50^{\circ}\text{C}$ ) or corrosive liquids (i.e., acid-based  
10 pitch remover). The goal was to machine samples from the joint assemblies without deleteriously affecting the joint strength. The resulting flexural samples were nominally 3x4x45 mm, in accordance with the ASTM standard C1161-94 "Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature." The 4x45 mm faces of the flexural specimens were ground with 20  
15  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  grinding media before flexural strength tests were conducted.

Flexural strength testing was conducted in accordance with ASTM standard C1161-94. Flexural strength was measured for Zerodur® - Zerodur® joints that had been cured at room temperature, and those heat-treated at 60, 90, or 120°C for 20 h. The flexural strength of monolithic Zerodur® was also measured for  
20 comparative purposes (note that the monolithic Zerodur® flexural surfaces were also prepared with a 20  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  grinding media).

The results from the flexural strength testing are shown in Figure 4. The average flexural strength of the Zerodur® - Zerodur® joints was greater than 5,000 psi, regardless of the heat-treatment temperature. However, the Zerodur® - Zerodur® joints always yielded a lower flexural strength than the monolithic Zerodur® samples, which had an average flexural strength of >13,000 psi. A flexural strength of 5000 psi is more than six times greater than the allowable working stress (750 psi), and more than three times greater than the ultimate handling stress (1,500 psi) for Zerodur®. Thus, Zerodur® - Zerodur® joints prepared by the low temperature joining process and heat treated at temperatures ranging from 60 to 120°C are expected to be suitably strong for use light-weighted Zerodur® mirror blanks.

### Example 2

The CTE of components joined according to the present invention is most preferably the same as that of monolithic glass ceramic materials. The minimization or elimination of joint-induced CTE variation ensures dimensional stability when the mirror-blank is used for applications, such as remote sensing.

Testing was conducted to determine whether a composite glass ceramic joint has the same CTE as monolithic glass ceramics. All samples intended for CTE evaluation were obtained from the same slab of Zerodur® (Melt Number F-9831). The intrinsic variation of CTE in the slab was determined by measuring the CTE at three positions. The three values of CTE were -33, -25 and -20 ppb/K

(each CTE reported herein is an average value, measured from 0 to 50°C). Note that the typical measurement accuracy for the CTE in the temperature range of 0 to 50°C is  $\pm 10$  ppb/K and the precision under repeatability conditions is  $\pm 5$  ppb/K. Therefore, the average CTE of the Zerodur® slab from 0 to 50 °C (Melt Number F-9831) was  $-26 \pm 10$  ppb/K.

Samples with the nominal dimensions of 60x25x25 mm were used to prepare Zerodur® - Zerodur® joint assemblies for CTE evaluation. These samples were cleaned and joined using the same procedures described in the Mechanical Strength section (above). Two Zerodur® - Zerodur® joint assemblies were prepared for CTE evaluation and allowed to cure for at least 7 days at room temperature. A CTE rod (6 mm diameter) was core drilled from each of the two joint assemblies, as shown in Figure 8.

The CTE of the first rod was measured before and after 20 hour heat-treatments at 60, 100 and 120°C, while the CTE of the second rod was measured before and after 20 hour heat-treatments at 60, 90 and 120°C. Figure 4 compares the CTE data collected from each of the joined CTE rods with the average CTE of the Zerodur<sup>TM</sup> slab (melt number F-9831). Note that all CTE data are within 10 ppb/K of the average CTE measured for the Zerodur® slab. Thus, the low temperature joining process does not affect CTE, and when the process according to the present invention is used to fabricate light-weighted Zerodur® mirror blanks, remarkably superior and stable composite structures are formed.

### Example 3

One general procedure that can be used to prevent the silicate-containing joining liquid from prematurely drying prior to bonding is as follows.

Strong bonds between Zerodur® pieces were made in a class 100 clean  
5 box with humidity control ( $\pm 2\%$  Relative Humidity) at ambient temperature. In  
one experiment, a polished face plate and polished back plate were jointed to a  
latticed 2-part polished rib structure assembled with slots as shown in Figure 1D.  
In a second experiment, a water-jet cut light-weighted core was joined to a  
polished face plate and polished back plate. The bonding surface of the core was  
10 coarse ground. The face plate had four ventilation holes as illustrated in Figure  
1B to allow dehydration of the joints. In a third experiment, 3mmx4mmx45mm  
parallepipeds were joined on a 4mmx45mm fine ground side to a polished plate.  
The relative humidity was varied from 25-90% R.H. at ambient temperature. The  
time period between solution application and bonding was varied as well from  
15 immediately after application to 10 min. after application.

At RH values of 30% and higher, the joints were excellent, *e.g.*, at RH less than  
30%, the joints had imperfections.

The preceding examples can be repeated with similar success by  
substituting the generically or specifically described reactants and/or operating  
20 conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain  
the essential characteristics of this invention and, without departing from the

spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

We claim:

1. A low-temperature process for the fabrication of lightweight composite glass ceramic structures, comprising:

providing a plurality of glass ceramic components, said glass ceramic  
5 components each being polished to form at least one joining surface on each component,

providing a silicate-containing joining liquid to at least one of the joining surfaces,

bringing the joining surfaces of the plurality of glass components together  
10 to form a joint,

allowing the joint to cure for a period of time of at least 20 hours at a temperature of at least 20 degrees C, whereby a cured joint is formed between said plurality of glass components, and

dehydrating the cured joint gradually by raising the temperature slowly  
15 and maintaining an elevated temperature below the glass transition temperature of the glass ceramic for at least 20 hours.

2. A method as claimed in claim 1, wherein the step of dehydrating comprises gradually raising the temperature at a rate which allows dehydration of the joint  
20 without imparting damage to the joint from accelerated H<sub>2</sub>O evaporation.



3. A process as claimed in claim 1, wherein the glass ceramic components are Zerodur® components.
4. A process as claimed in claim 1, wherein the glass ceramic components  
5 include a low expansion material prepared by partially ceramizing a lithium alumino silicate glass.
5. A process as claimed in claim 1, wherein the glass ceramic components include a material selected from the group consisting of Nexcera, Clearceram,  
10 VO<sub>2</sub>, Astrosital and Sitall.
6. A process as claimed in claim 1, wherein the silicate containing liquid is a lithium silicate containing liquid or a sodium silicate containing liquid.
- 15 7. A process as claimed in claim 1, wherein the silicate containing liquid is an alkali silicate, alkaline earth silicate, mixed alkali silicate, mixed alkaline earth silicate, or mixed alkali/alkaline earth silicate liquid.
8. A process as claimed in claim 2, wherein the step of gradually raising the  
20 temperature comprises increasing the temperature at a rate less than or equal to 3 degrees K/hour.

9. A process as claimed in claim 8, wherein the temperature is periodically stabilized and held.
10. A process as claimed in claim 9, wherein the temperature is stabilized at  
5 intervals of from 5 to 20 degrees C and held for at least 10 hours.
11. A process as claimed in claim 10, wherein the temperature is stabilized at intervals of about 10 degrees C and held for about 20 hours.
- 10 12. A process as claimed in claim 1, wherein the components include at least one component with a hollowed out light-weighted portion.
13. A process as claimed in claim 1, wherein the components comprise segments of a light-weighted core.
- 15 14. A process as claimed in claim 1, wherein the components include a mirror blank.
15. A process as claimed in claim 1, wherein the period of time is at least one  
20 hour.

16. A process as claimed in claim 1, wherein the period of time is at least one day.

17. A process as claimed in claim 1, wherein the period of time is at least one  
5 week.

18. A process as claimed in claim 1, wherein the step of providing the silicate containing liquid comprises applying the silicate containing liquid in an amount of at least 0.01 microliter /cm<sup>2</sup>.

10

19. A process as claimed in claim 2, wherein the temperature is from 60 to 600 degrees C.

20. A process as claimed in claim 19, wherein the temperature is below 120  
15 degrees C.

21. A glass ceramic composite, comprising:

a plurality of glass ceramic components, said components being rigidly connected by a silicate-containing layer formed by curing a silicate-containing  
20 liquid between the glass ceramic components at a temperature of at least 20 degrees C for at least 20 hours.

22. A glass ceramic composite as claimed in claim 21, wherein the cured silicate-containing layer is dehydrated at a temperature at or below 600 degrees C.
23. A glass ceramic composite as claimed in claim 22, wherein the cured silicate-  
5 containing layer is dehydrated at a temperature at or below 120 degrees C.
24. A glass ceramic composite as claimed in claim 21, wherein the plurality of glass ceramic components comprise Zerodur components.
- 10 25. A glass ceramic composite as claimed in claim 21 wherein the plurality of glass ceramic components include a glass ceramic material prepared by partially ceramizing a lithium alumino silicate glass.
26. A glass ceramic composite as claimed in claim 20, wherein the plurality of  
15 glass ceramic components include a material selected from the group consisting of Nexcera, Clearceram, VO<sub>2</sub>, Astrositall and Sitall.
27. A glass ceramic composite as claimed in claim 21, wherein at least one of the glass ceramic components contains a hollowed out space.
- 20 28. A glass ceramic composite as claimed in claim 21, wherein at least one of the components comprises a mirror blank.

29. A glass ceramic composite as claimed in claim 21, wherein the light weighted section is prepared by assembling separate segments of glass ceramic.

30. A glass ceramic composite as claimed in claim 16, wherein the rigid  
5 connection can withstand tensile stresses during usage of at least 750 psi.

31. A mirror blank suitable for use in space or flight applications comprising a plurality of glass ceramic components joined by a silicate-containing liquid and cured at a temperature of at least 20 degrees C.

10

32. A mirror blank as claimed in claim 31, wherein the mirror blank is formed from a face plate, a back plate, and at least one supporting element.

33. A mirror blank as claimed in claim 32, wherein there are a plurality of  
15 supporting elements.

34. A mirror blank as claimed in claim 33, wherein the plurality of supporting elements comprise crossed vertical walls, said vertical walls being provided with slots to form a lattice.

20

35. A mirror blank as claimed in claim 34, wherein each lattice opening forms a cell, and the cell is provided with a ventilation hole or is open to the surrounding environment.
- 5 36. A composite glass ceramic structure suitable for use as a microlithography stage comprising a plurality of glass ceramic components joined by a silicate-containing liquid and cured at a temperature of at least 20 degrees C.
37. A method of joining lightweight composite glass ceramic surfaces
- 10 comprising applying to at least one of said surfaces a silicate-containing solution and curing for an extended period at a slightly elevated temperature above room temperature.
38. A method as claimed in claim 37, wherein the temperature is from 30 to 50
- 15 degrees C, and the extended period is at least 20 hours.
39. A glass ceramic composite as claimed in claim 21, wherein said silicate-containing layer comprises, in weight %,
- H<sub>2</sub>O 50-99.9
- 20 SiO<sub>2</sub> 0.01-40
- Al<sub>2</sub>O<sub>3</sub> 0-10
- Li<sub>2</sub>O 0-20

Na<sub>2</sub>O 0-20  
K<sub>2</sub>O 0-25  
MgO 0-10  
CaO 0-10  
5 BaO 0-10  
SrO 0-10.

40. A light weight glass-ceramic mirror blank, comprising:  
a face plate which is circular in shape,  
10 a back plate which corresponds in shape and size to the face plate,  
a plurality of support elements located between said face and back plates,  
said plurality of supporting elements forming a latticework  
said latticework and face plate and back plate defining a plurality of cells,  
said cells each being provided with a ventilation aperture or being open to  
15 the environment,  
said face plate, plurality of supporting elements, and back plate being  
joined by a silicate-containing liquid in a plurality of joining steps to form a  
plurality of joints, and at each step, the joint cured at a temperature of at least 20  
degrees C for a period of at least 20 hours.

20

41. A mirror blank as claimed in claim 1, wherein the joint is further dehydrated  
at a temperature of from 30 to 50 degrees C for at least 20 hours.

42. An optical or electrooptical device comprising a composite of claim 21.

43. A device of claim 42 which is an etalon.

5

44. A vacuum chamber comprising a composite of claim 21.

45. A composite of claim 21 which has a low coefficient of expansion.

10 46. A low-temperature process for the fabrication of a lightweight composite glass ceramic structure, comprising:

providing at least two surfaces at least one of which is a glass ceramic, and the other of which is a glass-ceramic or another material having a surface group which reacts with a silicate joining liquid to form a stable bond, said surfaces  
15 each being polished to form joining surfaces on each,

providing a silicate-containing joining liquid to at least one of the joining surfaces,

bringing the joining surfaces together to form a joint,

allowing the joint to cure for a period of time of at least 20 hours at a  
20 temperature of at least 20 degrees C, whereby a cured joint is formed between said surfaces, and



dehydrating the cured joint gradually by raising the temperature slowly and maintaining for at least 20 hours an elevated temperature below the lowest temperature at which one of the joined components is adversely affected.

5        47. A process of claim 46 wherein at least one of the surfaces is SiO<sub>2</sub>, quartz, Al<sub>2</sub>O<sub>3</sub>, multi component silicate glass, BK-7, ULE, antimony silicate glass, a low expansion metallic alloy, optionally coated with a thin layer of SiO<sub>2</sub>, germanium glass, tellurium glass or borosilicate glass.

10        48. A process of claim 46 where at least one of the surfaces is a glass and said elevated temperature is below the lowest glass transition temperature of said joined surfaces.

15        49. A process as claimed in claim 46, wherein the glass ceramic component is a Zerodur® component.

50. A glass ceramic composite, comprising:  
at least two surfaces at least one of which is a glass ceramic and the other  
20 of which is a glass-ceramic or another material having a surface group which reacts with a silicate joining liquid to form a stable bond, said surfaces being rigidly connected by a silicate-containing layer formed by curing a silicate-

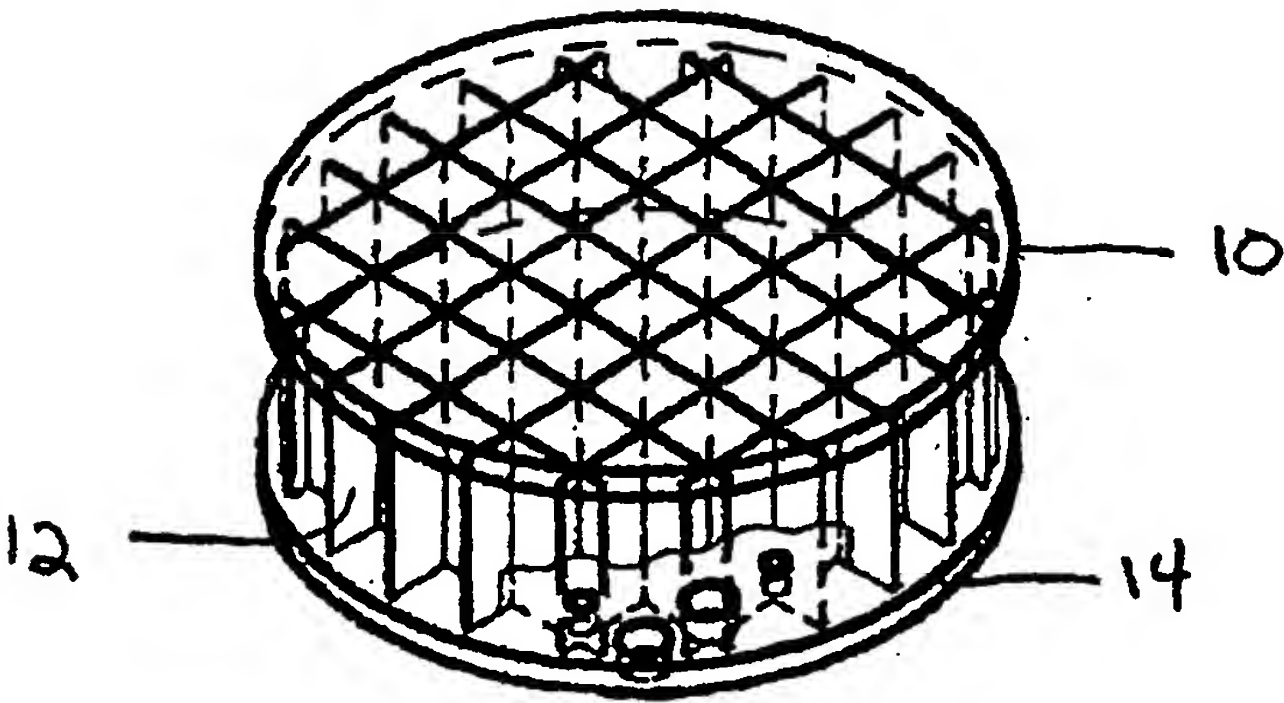
containing liquid between the glass ceramic surface and said other surface at a temperature of at least 20 degrees C for at least 20 hours.

51. A glass ceramic composite as claimed in claim 21, wherein the glass  
5 ceramic surface comprises Zerodur®.

52. A glass ceramic composite of claim 21 wherein said other surface is SiO<sub>2</sub>,  
quartz, Al<sub>2</sub>O<sub>3</sub>, multi component silicate glass, BK-7, ULE, antimony silicate glass,  
a low expansion metallic alloy, optionally coated with a thin layer of SiO<sub>2</sub>,  
10 germanium glass, tellurium glass or borosilicate glass.

53. A process of claim 46 wherein said joining liquid comprises ground or  
fritted silica-containing glass-ceramic or glass.

FIG 1A



5

FIG 1B

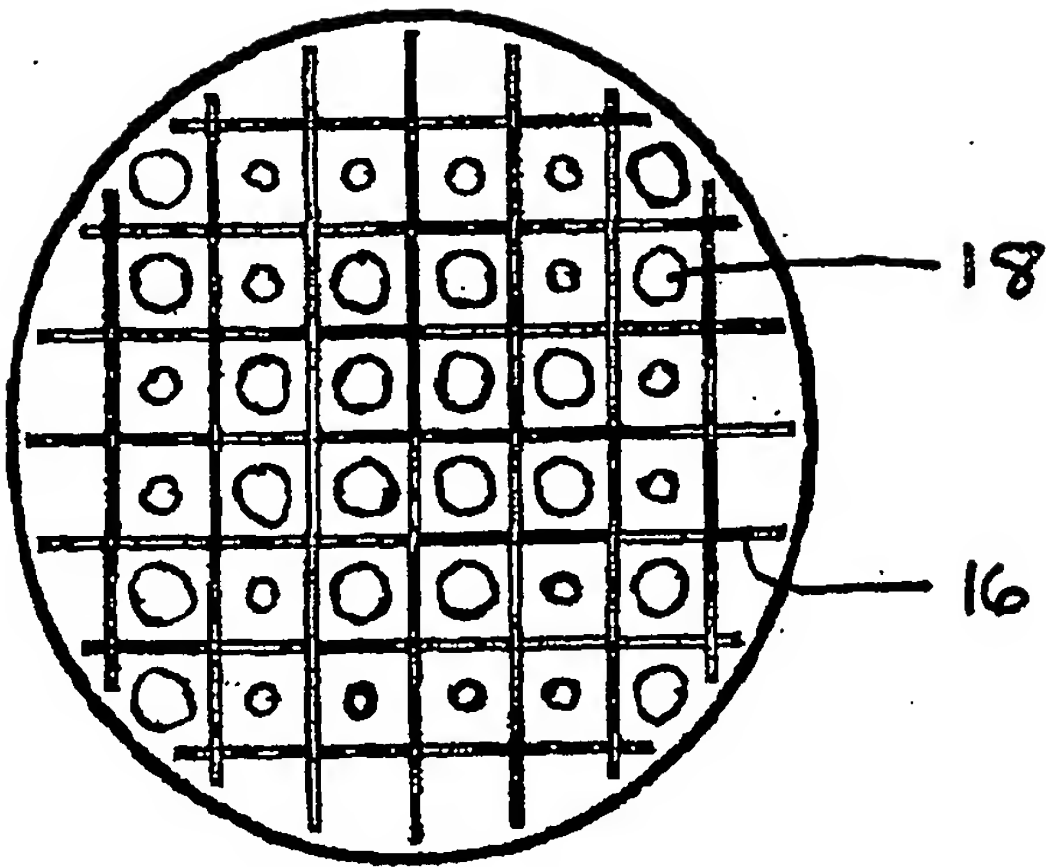
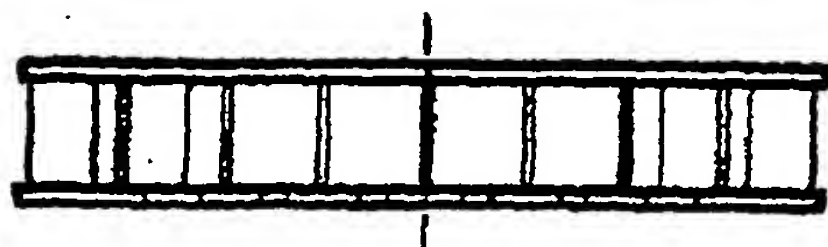
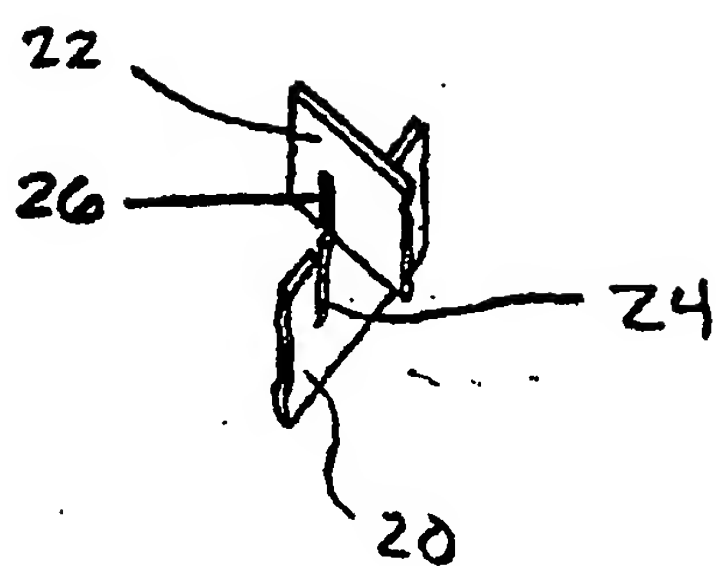


FIG 1C



5

FIG 1D



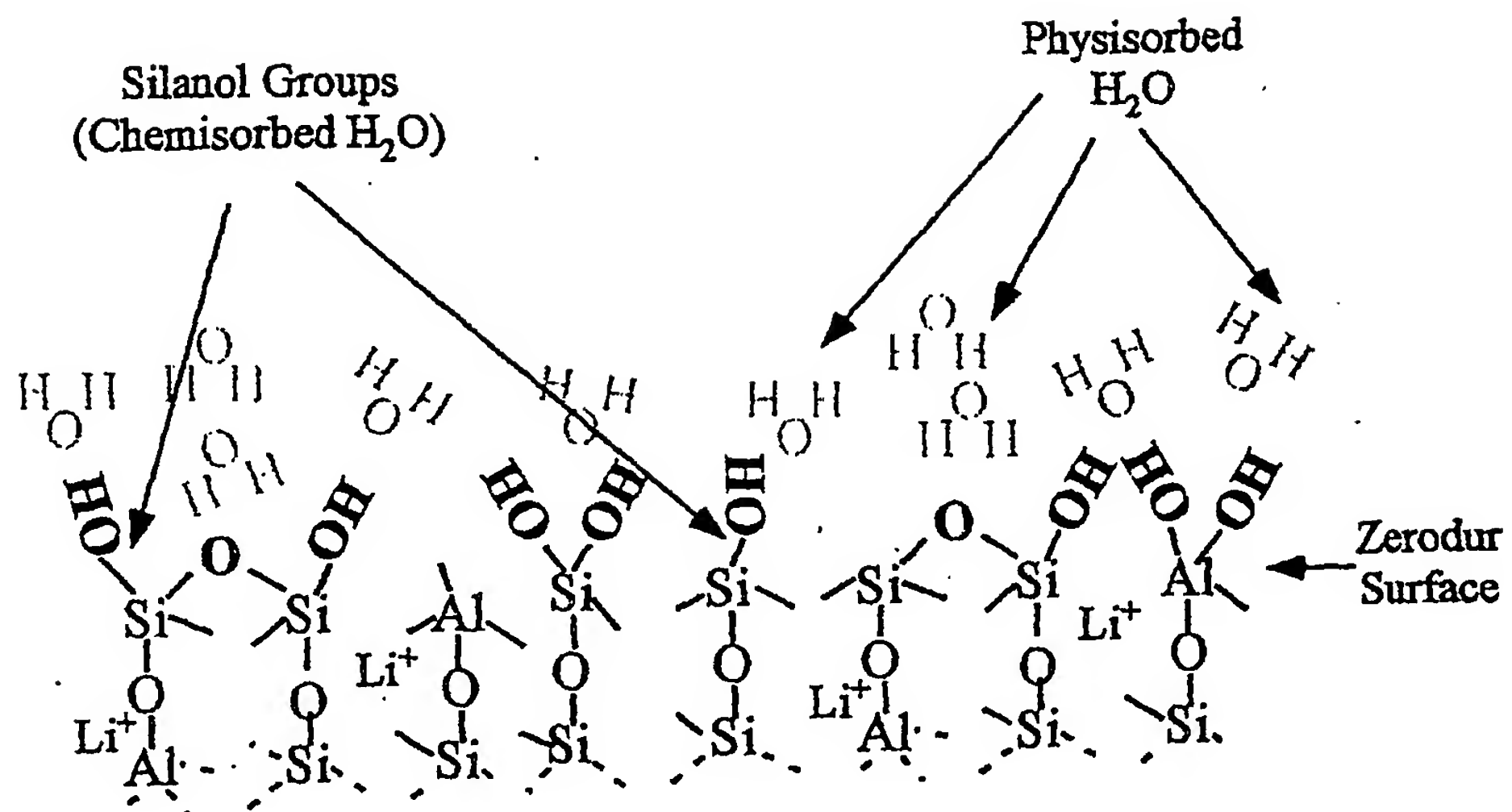
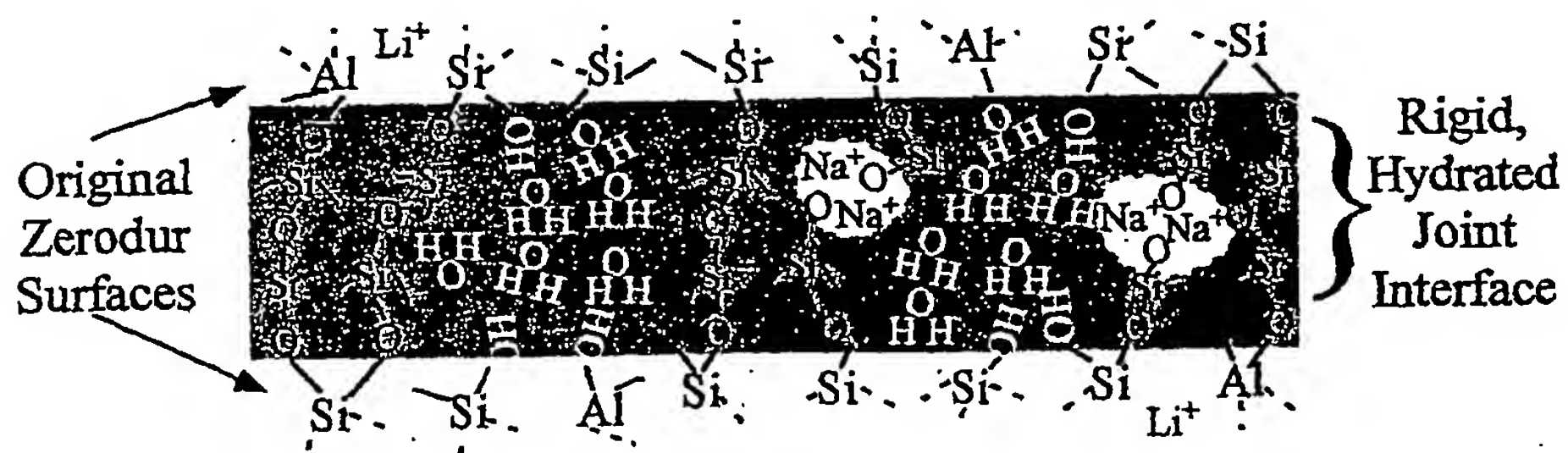


FIG 2



5

FIG 3

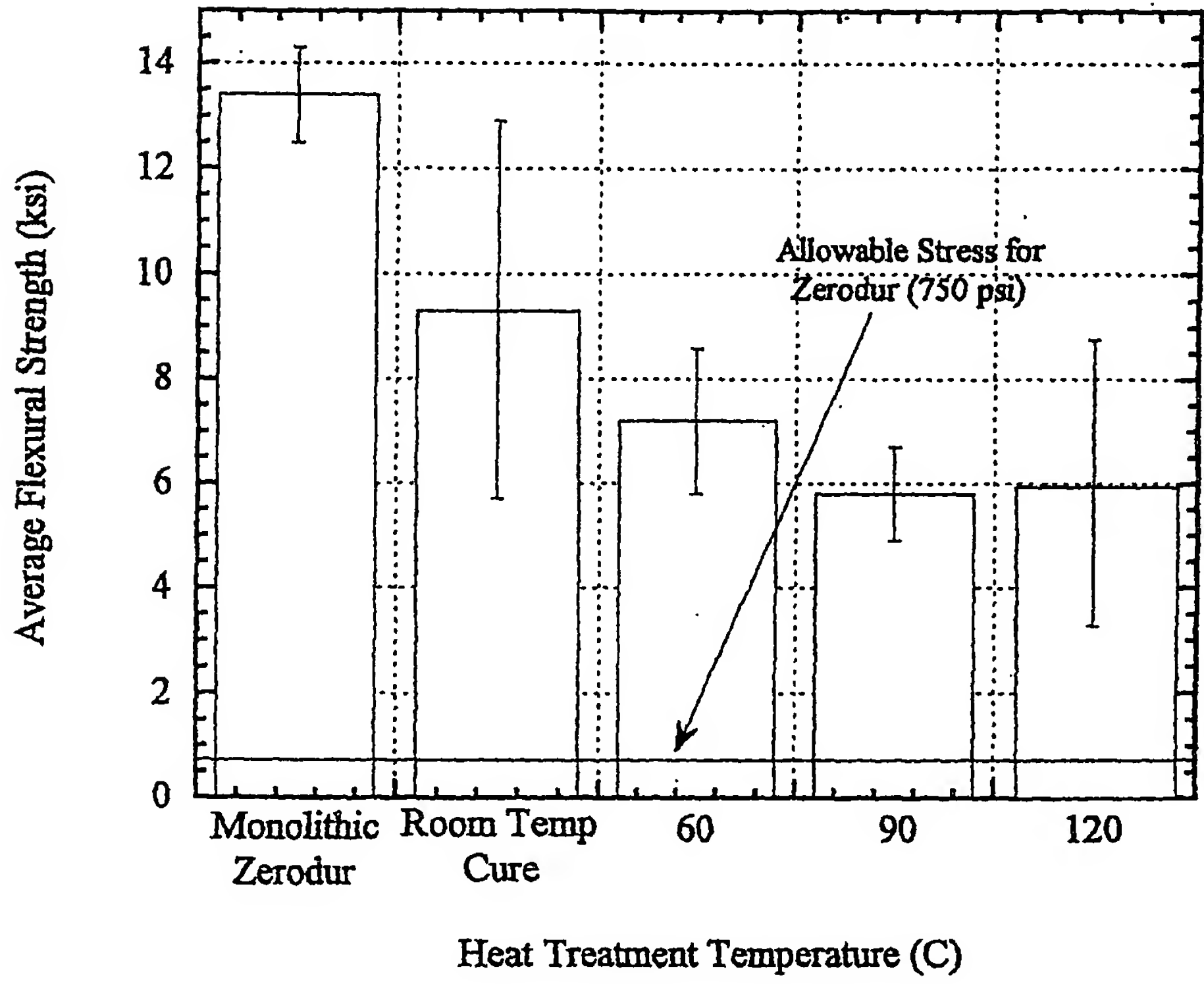


FIG 4

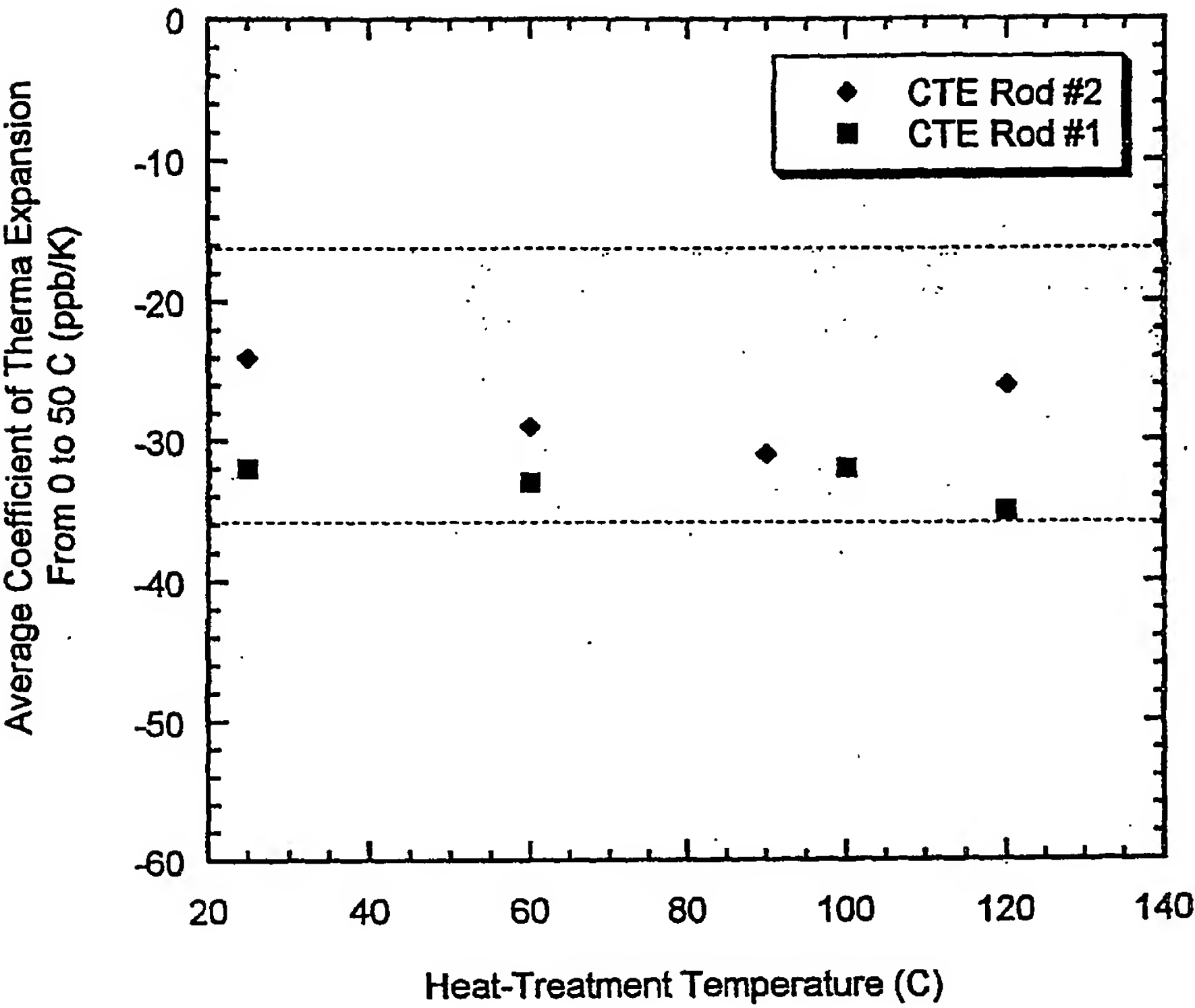


FIG 5

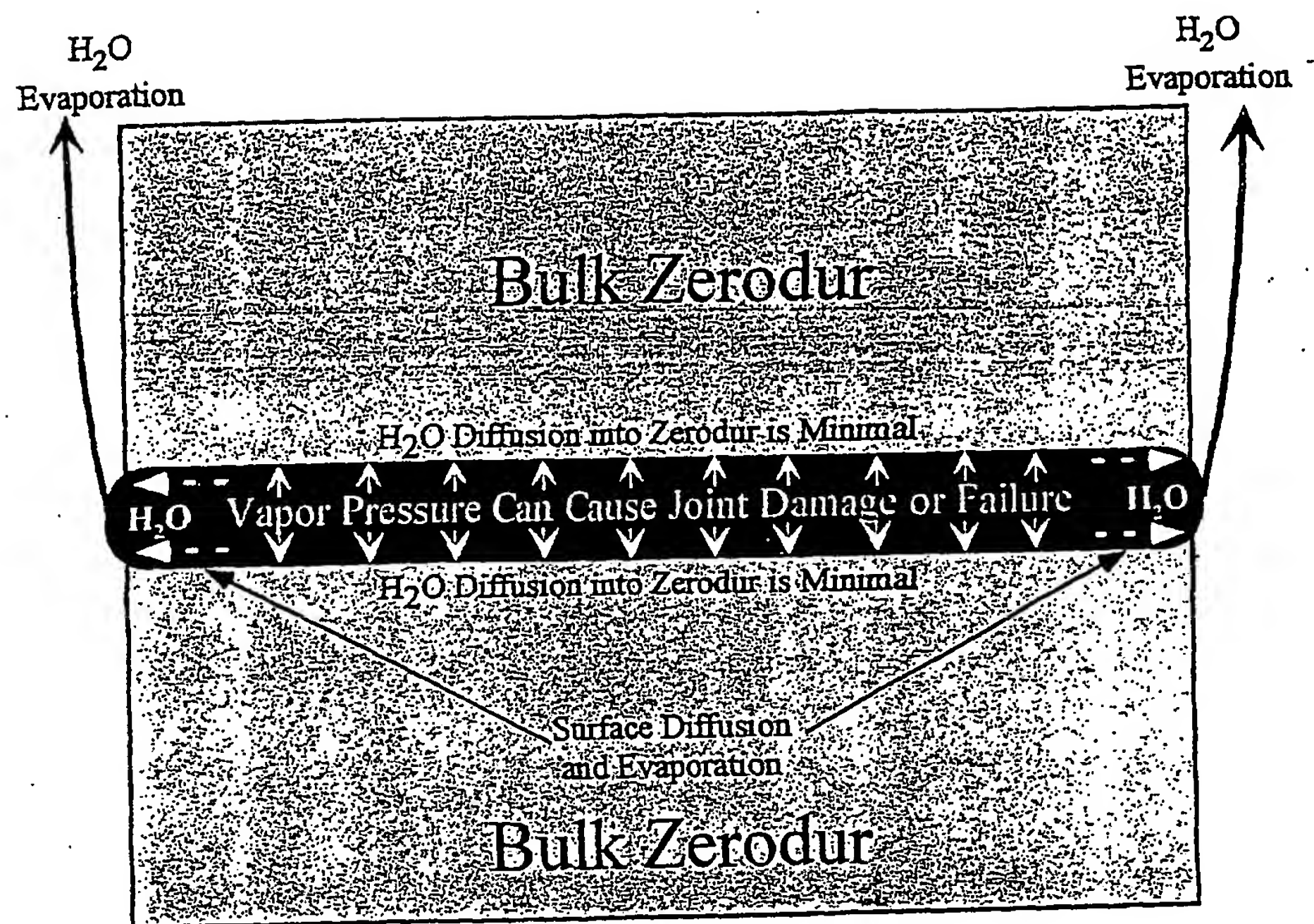


FIG 6



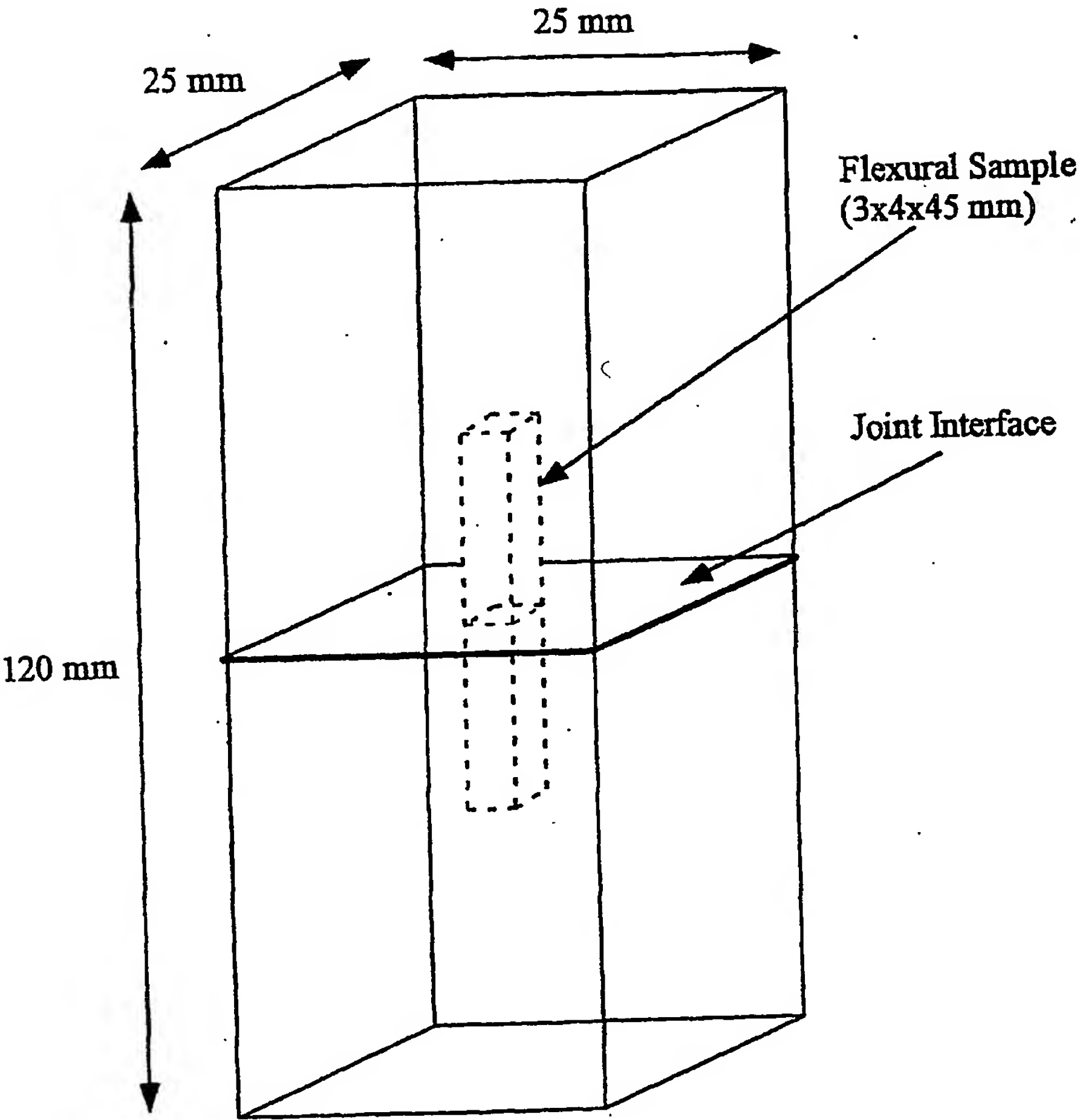


FIG 7

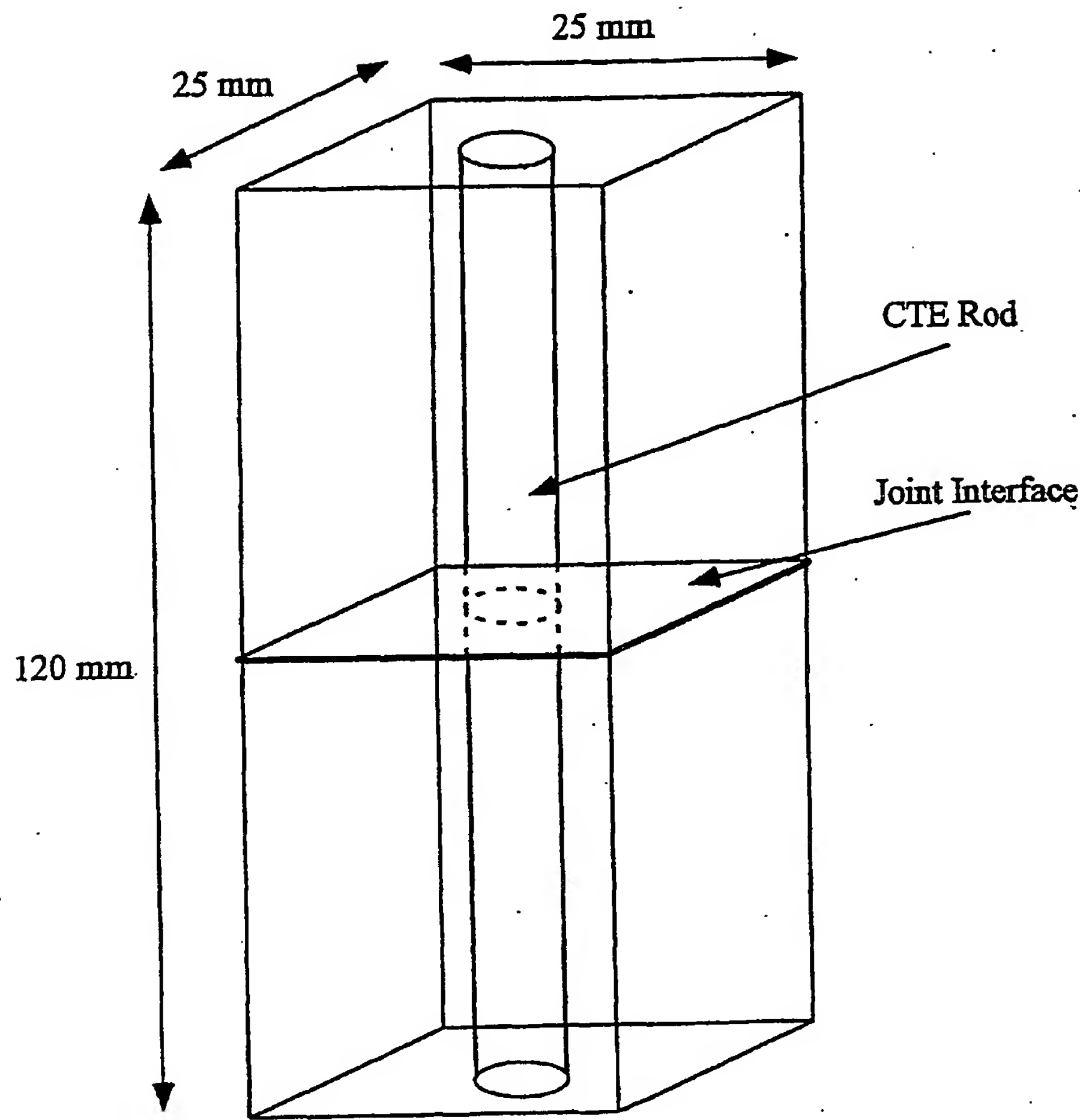


FIG 8

## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 01/41042

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C03C27/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 43117 A (LOCKHEED MARTIN ENERGY SYS INC) 20 November 1997 (1997-11-20) abstract page 1, line 6 - line 11 page 3, line 24 -page 4, line 5 page 6, line 24 -page 7, line 25 example page 23, line 7 - line 12 claims 1,5,18,21	1-53
A	DE 197 31 075 A (INST MIKROTECHNIK MAINZ GMBH) 21 January 1999 (1999-01-21) abstract column 2, line 13 - line 25 column 2, line 40 - line 44 column 2, line 57 - line 68	1-53

---  
-/--



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

19 October 2001

Date of mailing of the international search report

26/10/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Grenette, S

# INTERNATIONAL SEARCH REPORT

Inter Application No  
PCT/US 01/41042

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>TIETZE H ET AL: "UPDATE OF RECENT DEVELOPMENTS FOR LIGHTWEIGHT LARGE MIRROR BLANKS OF ZERODUR" ADVANCED TECHNOLOGY OPTICAL TELESCOPES III.;TUCSON, AZ, USA, vol. 628, 1986, pages 512-517, XP001033428 Proceedings of SPIE - The International Society for Optical Engineering 1986 SPIE, Bellingham, WA, USA page 513, welded honeycomb core paragraph -----</p>	1-53

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/41042

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 9743117	A	20-11-1997	AU	3137097 A		05-12-1997
			WO	9743117 A1		20-11-1997
			US	6129854 A		10-10-2000
DE 19731075	A	21-01-1999	DE	19731075 A1		21-01-1999